Monitoring of dl-POPs and PFOS and its precursors in air – Asia-Pacific region

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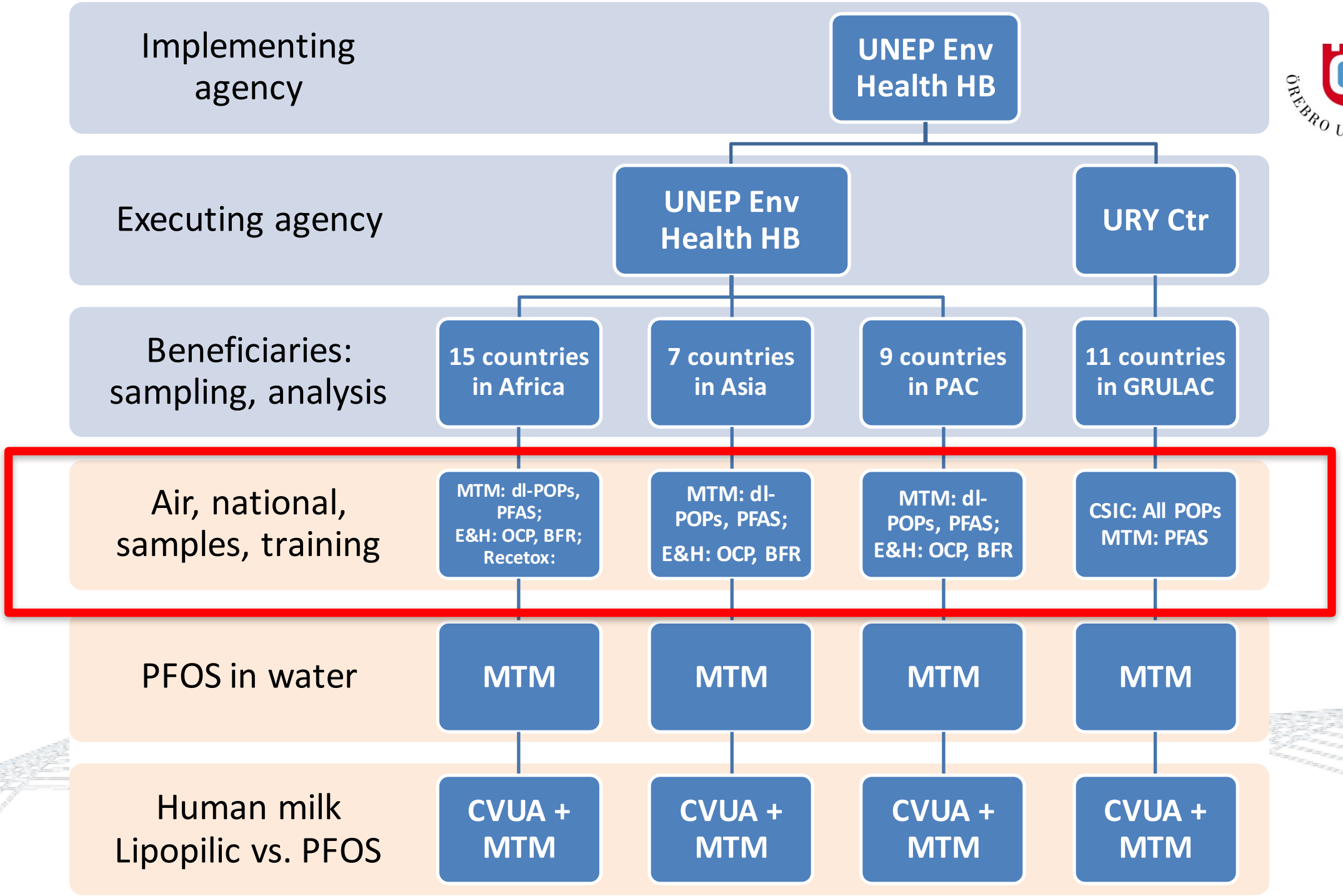
Content

- Context
- Sampling
  - Procedures and status of samples received
- Analysis
  - First results for dl-POPs
- Next steps
- Conclusions


Implementing agency
UNEP Env Health HB
Executing agency
UNEP Env Health HB
URY Ctr
Beneficiaries: sampling, analysis
15 countries in Africa
7 countries in Asia
9 countries in PAC
11 countries in GRULAC
Air, national, samples, training
MTM: dl-POPs, PFAS; E&H: OCP, BFR; Recetox:
MTM: dl-POPs, PFAS; E&H: OCP, BFR
MTM: dl-POPs, PFAS; E&H: OCP, BFR
CSIC: All POPs MTM: PFAS
PFOS in water
MTM
MTM
MTM
MTM
Human milk Lipopilic vs. PFOS
CVUA + MTM
CVUA + MTM
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MTM's role related to the core matrix air in the African region

- MTM Research Centre has been contracted by UNEP (now UN Environment) as expert laboratory for the analysis of dioxin-like POPs and perfluorooctane sulfonate (PFOS) and relevant precursors in air;
- This includes:
  - Technical advice for sampling and analysis of these POPs in air;
  - Analysis of PUFs from passive air samplers (PUF-5, PUF-7; PUF-11) for dl-POPs and PFOS;
  - Analysis of PUF/XAD from two active air samplers (Mongolia and Vietnam) for dl-POPs and PFOS;
  - On-site training of POPs laboratories in Asia-Pacific region (Thailand, Vietnam);
- The duration of the sampling activities are during two years (2017-01 until 2018-12);
- The majority of the chemical analysis to be performed in 2018 and 2019.

Sampling scheme for PAS/PUF in UNEP/GMP2 projects

Assignment of samplers, PUFs, and analytes according to laboratory per country)			No. analyses per year
Sampler 1:	PUFs 1-4:	For basic POPs pesticides in expert back-up laboratory	4
		drins, chlordanes, DDTs, HCHs, heptachlors, mirex, HCB, pentachlorobenzene, endosulfans,	
		toxaphenes, chlordecone	toxaphene, annual sample only
Sampler 2:	PUFs 1-4:	For basic POPs in national POPs laboratory	4
		drins, chlordanes, DDTs, HCHs, heptachlors, mirex, HCB, pentachlorobenzene, endosulfans,	
		toxaphenes, chlordecone	toxaphene, annual sample only
Sampler 3:	PUFs 1-4:	For indicator PCB in expert back-up laboratory	4
		6 indicator PCB	
Sampler 4:	PUFs 1-4:	For indicator PCB in national POPs laboratory	4
		6 indicator PCB	
Sampler 5:	PUFs 1-4:	For dioxin-like POPs in expert back-up laboratory (combined into one extract as annual average)	1
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 6:	PUFs 1-4:	For dioxin-like POPs in national dioxin laboratory (combined into one extract as annual average)	1
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 7:	PUFs 1-4:	For dioxin-like POPs in expert back-up laboratory (each exposure to generate one seasonal data point; total of 4 per year and country)	4
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 8:	PUFs 1-4:	For dioxin-like POPs in national laboratory (each exposure to generate one seasonal data point; total of 4 per year and country)	4
		17 PCDD/PCDF, 12 dl-PCB	
Sampler 9:	PUFs 1-4:	For PBDE in expert laboratory	4
		8 PBDE, HBCD, PBB	
Sampler 10:	PUFs 1-4:	For PBDE in national laboratory	4
		8 PBDE, HBCD, PBB	
Sampler 11:	PUFs 1-4:	For PFOS in expert laboratory	4
		6 PFAS	
Sampler 12:	PUFs 1-4:	For PFOS in national laboratory	4
		6 PFAS	

Color codes:

Green Analysis in expert back-up laboratory

No Fill Analysis in national laboratory

Yellow Groups of chemicals recommended for analysis

PUFs cleaned with water and acetone and conditioned to capture groups of POPs were provided by Recetox as follows:

- Conditioning with dichloromethane (DCM) for: OCPs, indicator PCB, PBDE+HxBB+HBCD ⇒ E&H VU
- Conditioning with toluene for: dl-POPs ⇒ MTM
- Conditioning with methanol for: PFOS+ ⇒ MTM

Status of samples received - 2017

		Sample ID	Sample ID	Sample ID	Date arrived	Sample ID	Sample ID	Sample ID	Date arrived	Sample ID	Sample ID	Sample ID	Date arrived	Sample ID	Sample ID	Sample ID	Date arrived	Subtotal
Asia		PUF 5	PUF 7	PUF 11		PUF 5	PUF 7	PUF 11		PUF 5	PUF 7	PUF 11		PUF 5	PUF 7	PUF 11		
Cambodia	KHM	Void		Void		Void		Void		Void		Void						0
Indonesia	IDN	Void		Void		Void		Void		Void		Void		Void		Void		0
Lao PDR	LAO	Void		Void		Void		Void		Void		Void		LAO-5 (2017-IV)		LAO-11 (2017-IV)	2018-03-16	2
Mongolia	MNG	Void	Void	Void		MNG-5 (2017-II)	Void	MNG-11 (2017-II)	2017-10-24	MNG-5 (2017-III)	Void	MNG-11 (2017-III)	2017-10-24	MNG-5 (2017-IV)		MNG-11 (2017-IV)	2018-05-16	6
Phillipines	PHL	Void		Void		Void		Void		Void		Void						0
Thailand	THA	Void		Void		Void		Void		Void		Void		THA-5 (2017-IV)		THA-11 (2017-IV)	2018-06-07	2
Vietnam	VNM	Void	Void	Void		VNM-5 (2017-II)	VNM-7 (2017-II)	VNM-11 (2017-II)	2017-10-23	VNM-5 (2017-III)	VNM-7 (2017-III)	VNM-11 (2017-III)	2017-10-23	VNM-5 (2017-IV	VNM-7 (2017-IV	VNM-11 (2017-IV)	2018-01-15	9
Asia subtotal	7	0	0	0	0	2	1	2	2	2	1	2	2	4	1	4	4	19

Summary 2017: 19 of 64 expected PUFs were received, corresponding to 30%.
MNG was scheduled for dl-POPs analysis but does not have received PUFs-7 ⇒ revise plan as to PUF-7?

PUF-5, PUF-7: Analysis for dl-POPs – MTM lab lacks sensitivity and selectivity to analyse air samples
⇒ MTM entered into agreement with CSIC to analyse PUFs for dl-POPs
PUFs were analyzed for each season

PUF-11: Analysis for PFOS and precursors
⇒ analytical method almost finalized to analyse PUFs for PFOS and precursors
(unexpected difficulties with precursor compounds and some background issues
Note: in 3rd interlab – no consensus values could be assigned for FOSAs and FOSEs among experienced laboratories).

Status of samples received - 2018

Country name	ISO_3	Campaign 1				Campaign 2				Campaign 3				Campaign 4				Year 2018
		Sample ID	Sample ID	Sample ID	Date arrived	Sample ID	Sample ID	Sample ID	Date arrived	Sample ID	Sample ID	Sample ID	Date arrived	Sample ID	Sample ID	Sample ID	Date arrived	Subtotal
Asia		PUF 5	PUF 7	PUF 11		PUF 5	PUF 7	PUF 11		PUF 5	PUF 7	PUF 11		PUF 5	PUF 7	PUF 11		
Cambodia	KHM	KHM-5 (2018-I)		KHM-11 (2018-I)	2018-07-16	KHM-5 (2018-II)		KHM-11 (2018-II)	2018-07-16									4
Indonesia	IDN	IDN-5 (2018-I)		IDN-11 (2018-I)	2018-03-06	IDN-5 (2018-II)		IDN-11 (2018-II)	2018-07-05									4
Lao PDR	LAO					LAO-5 (2018-II)		LAO-11 (2018-II)	2018-08-02									2
Mongolia	MNG	MNG-5 (2018-I)		MNG-11 (2018-I)	2018-05-16													2
Phillipines	PHL																	0
Thailand	THA	THA-5 (2018-I)		THA-11 (2018-I)	2018-06-07													2
Vietnam	VNM	VNM-5 (2017-I)	VNM-7 (2017-I)	VNM-11 (2017-I)	2018-04-26													3
Asia subtotal	7	5	1	5	5	3	0	3	3	0	0	0	0	0	0	0	0	17

Sampling still ongoing. Until to-date, 17 PUFs from an expected 64 PUFs have been received

Questions:

- From Indonesia, PUFs since 2018-I available – thank you; on track now.
- Philippines has not yet sent any PUF so far – status? Future procedure?
- From Lao: no PUFs from 2018-I; please check if one seasonis missing or wrong label.

No samples from active samplers received yet.

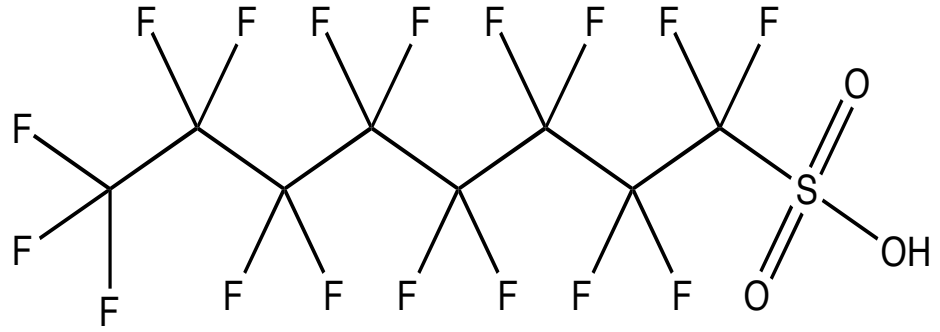
Preliminary results from PAS/PUF monitoring in Africa – dl-POPs

Concentrations in pg *per* PUF;
TEQs correspond to lower-bound values (LB);
i.e., <LOD = 0

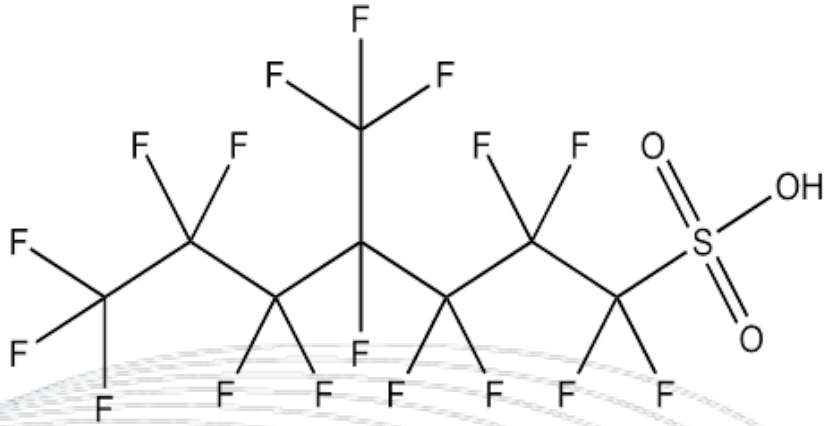
Note: for Ghana and Mali, there were two PUFs combined from the same season.

- PCDD/PCDF and dl-PCB were detected at low concentrations using 1 PUF for analysis
- Using 2 PUFs from the same season (where available) provides more material and more quantifiable congeners.

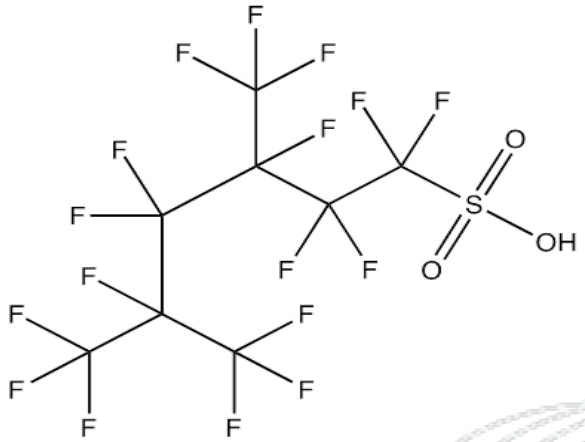
Perfluorooctane sulfonic acid (PFOS isomers)



L-PFOS

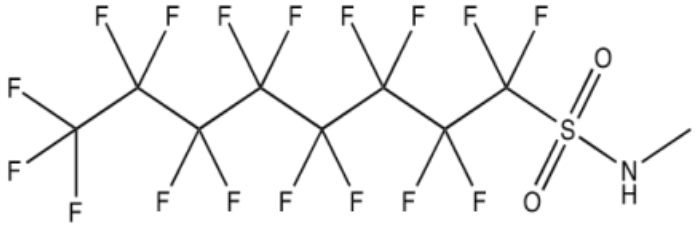


4-PFOS

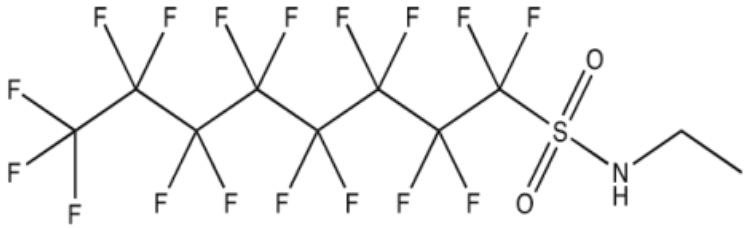


3,5-PFOS

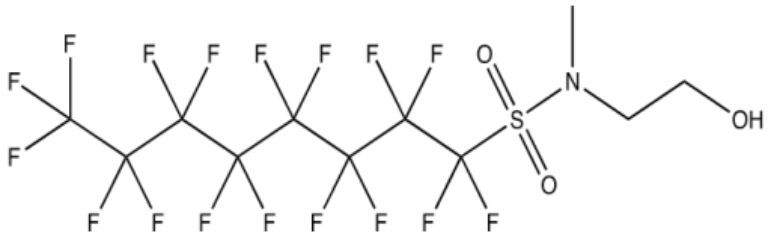
PFOS-related compounds



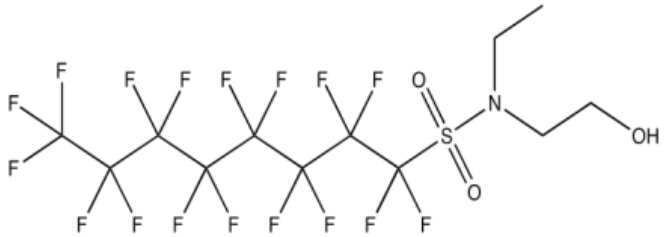
N-methyl perfluorooctane sulfonamide
MeFOSA



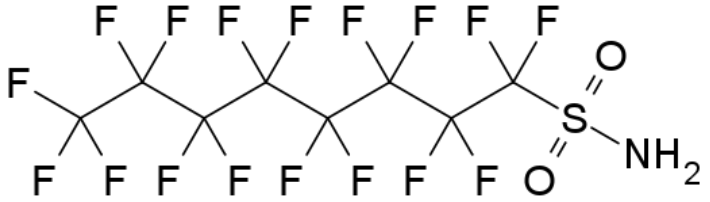
N-ethyl perfluorooctane sulphonamide
EtFOSA



N-methyl perfluorooctane sulfonamidoethanol
MeFOSE



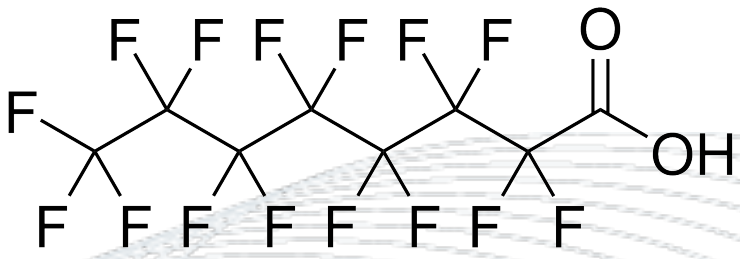
N-ethyl perfluorooctane sulfonamidoethanol
EtFOSE



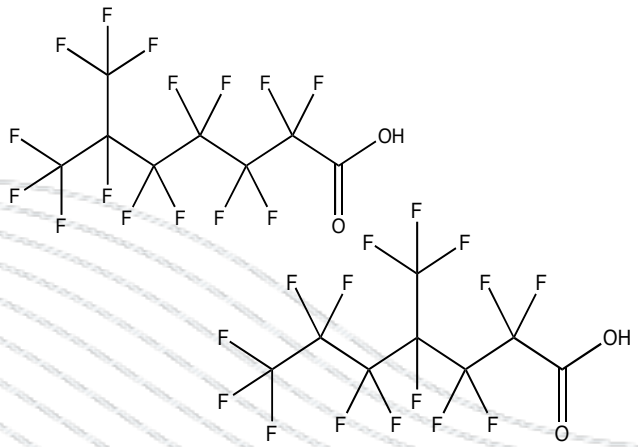
Perfluorooctanesulfonamide
FOSA

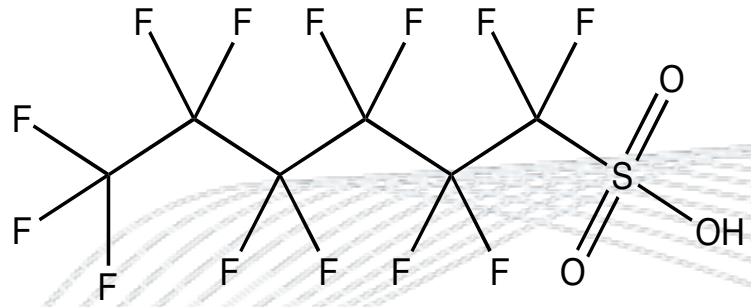
Next POPs? Analytes and matrices

	Air	Human Milk	Human Blood	Water
Perfluorooctanesulfonic acid (PFOS)	PFOS (linear and branched PFOS)			
POPs under review for listing				
Perfluorooctanoic acid (PFOA)	PFOA	PFOA	PFOA	PFOA
Perfluorohexanesulfonic acid (PFHxS)	PFHxS	PFHxS	PFHxS	PFHxS



Perfluorooctanoic acid





Perfluorohexane sulfonic acid

Conclusions and next steps

- Cleaned, conditioned PUFs for PAS provided by Recetox (minimum of 5 for countries without POPs laboratory; maximum of 12 for countries with basic POPs, dioxin and PFOS laboratories per campaign);
- PUFs from 2017 sampling received at 30%; arrival of 2018 PUFs ongoing (works well);
  - Need to have exact exposure dates and locations
  - GIS coordinates, temperature either from national information or retrieved from internet sources
- No samples from active air samplers in Asia yet received for chemical analysis;
- Method for analysis of PFOS and precursors still under development
  - We propose to include additional perfluorinated compounds – agreement from countries needed
- Analysis of dl-POPs through agreement between Örebro University and CSIC/Barcelona;
  - Analysis follows established methods. So far, concentrations of dl-POPs (very) low (quarterly samples).

Thank you